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Numerical Modeling of the Interactions of Oil, Marine Snow, and Riverine Sediments in the Ocean

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Abstract Natural or spilled oil in the ocean can interact with marine snow and sediment from riverine sources and form Marine Oil Snow (MOS) aggregates including aggregates consisting of phytoplankton, detritus, and feces. Such aggregates have a fractal structure and can transport oil from the surface layers to greater depths in the ocean, eventually settling on the seafloor. In recent studies of the Deepwater Horizon and IXTOC-1 oil spills in the Gulf of Mexico, this process was identified as one of the main mechanisms for transporting oil vertically in the water column. We have adapted a stochastic, one-dimensional numerical model that uses coagulation theory to simulate MOS formation and sinking in the ocean and predict the time evolution of physical properties and spatial distribution of MOS. Here we present the model development, calibration, and validation with measured MOS field data in the Gulf of Mexico during the Deepwater Horizon spill. We use a sensitivity analysis to identify critical parameters, and suggest future model improvements and areas where further experimental investigation is needed to improve our understanding of MOS formation and sedimentation. The model can be used during response and planning activities associated with oil spills in the marine environments.

1. Introduction

Accurate predictions of the transport and fate of oil spilled in the marine environment are important for response, clean up, and mitigation. Interest in these topics has increased since the Deepwater Horizon (DWH) spill in 2010, which released $7.79\times10^6$ L (4.9 million barrels) of oil into the Gulf of Mexico (GoM). Estimates from satellite imagery show that approximately $1.8\times10^5$ km$^2$ of the surface ocean was affected by spilled oil (Norse & Amos, 2010). However, not all of this oil reached or remained in the surface waters. Some percentage of oil sedimented to the seafloor; however, the amount is being debated. Yan et al. (2016) and Chanton et al. (2014) estimated that 1.6–2.6 $\times 10^7$ kg of petrocarbon accumulated on the seafloor after the DWH spill, amounting to approximately 3.0–4.9% of the total petrocarbon released. Studies of sediment samples around the DWH well site (Valentine et al., 2014) indicated that 4–31% of the oil sequestered in the deep ocean reached the seafloor. Recent studies by Stout and German (2017) and Stout et al. (2017) on the DWH sediments estimated that a total sedimented oil volume of 6.8–7.2% was not recovered during the DWH spill, while Romero et al. (2017) estimated that 21 $\pm$ 10% nonrecovered oil settled on the seafloor. Geochemical analysis of sediment cores in the DeSoto Canyon northeast of the DWH site suggests that some of the oil reached the seafloor in the form of large, heterogeneous aggregates.

Sedimentation of aggregates comprising oil and marine particles was observed during the DWH spill (Brooks et al., 2015; Passow, 2016; Passow & Ziervogel, 2016; Schwing et al., 2017), and some evidence exists for the formation of such aggregates during the IXTOC-1 oil spill in the southern GoM in 1979–1980 and during other oil spills (Daly et al., 2016; MOSSFA Report, 2014; Vonk et al., 2015). Observations following the DWH event of a flocculant layer covering deep corals (White et al., 2012), the effects on the benthos (Montagna et al., 2013), and distribution of geochemical tracers and settled sediments at the bottom (Stout et al., 2017; Valentine et al., 2014), suggest that at least some of this oil arrived at the seafloor within rapidly sinking aggregates of oil, biogenic, and mineral particles (Marine Oil Snow, MOS). However, such a transport mechanism is generally not included in models of oil transport and fate.
Marine snow are heterogeneous aggregates, >5 mm in size, consisting of phytoplankton, fecal pellets, microzooplankton, other organic detritus, and mineral particles (Alldredge & Silver, 1988). Maximum marine snow concentrations in near-surface waters were elevated in August 2010 (64.6 particles L\(^{-1}\)) compared with similar times in later years (2–20 particles L\(^{-1}\)), and abundances integrated over the top 140 m of the water column were up to an order of magnitude greater (Daly et al., 2016). The higher concentration of marine snow indicates the possibility of marine snow-oil interactions and the formation of MOS. Comparison of deep sediment trap data from August 2010 and October 2011 indicates enhanced fluxes of oil-derived hydrocarbons to the deep ocean facilitated by an extensive diatom bloom (Yan et al., 2016), although a fall bloom was a common occurrence at this station in later years, suggesting high interannual variability (Giering et al., 2017). This strongly suggests that marine snow formation and interactions between marine snow and oil in the surface waters can increase the vertical flux of oil to the seafloor.

Aggregation and sedimentation of oil with mineral and sediment particles has long been known to occur and has been extensively studied (Gong et al., 2014; Sterling et al., 2004; Sun & Zheng, 2009). However, large aggregates containing oil and biogenic material (phytoplankton, mucus, etc.) were also observed in the surface water and in sediment traps (Passow, 2016; Passow et al., 2012; Passow & Ziervogel, 2016). These MOS particles are thought to form by the aggregation of oil droplets with phytoplankton cells, marine snow particles, and transparent exopolymer particles (TEP) can lead to the rapid transport of oil from the surface waters to the seafloor, with sinking velocities estimated to be in the range 68–553 m d\(^{-1}\) (Passow et al., 2012).

Marine Oil Snow aggregates have been associated with large sedimentation events following oil spills (Daly et al., 2016; MOSSFA Report, 2014; Vonk et al., 2015), but they have yet to be included in models of oil in the environment. In this paper, we describe a new model of MOS formation and sedimentation. The one-dimensional (1-D) model incorporates biogenic and mineral particles as well as extracellular polysaccharides (mucus) and describes the evolution of the particle size spectrum throughout the water column, with comparisons made with in situ size spectra measured after the DWH oil spill. The model is able to trace the transport of multiple components of the MOS particles and can be used to help understand field and experimental observations, and for oil spill response, planning, and environmental risk assessment.

2. Model Development

The model uses coagulation theory to describe the evolution of the particle size spectrum of a collection of particles from multiple sources. Coagulation theory was developed by Von Smoluchowski (1916) and has been successfully used to tackle a variety of problems including particle size distributions in the oceans (Burd & Jackson, 2009; Jackson & Burd, 1998), atmospheric aerosol size distributions (Friendlander, 2000), and planet formation (Zsom & Dullemond, 2008). The theory uses three basic mechanisms for interparticle interactions: Brownian diffusion (which dominates for particles smaller than about 1 \(\mu m\), laminar and turbulent shear, and differential sedimentation where large, rapidly settling particles catch up and collide with smaller, slower settling particles (Burd & Jackson, 2009). The temporal evolution of the particle size spectrum \((n(m, t))\) in a homogeneous layer of water of thickness \(Z\) is given by

\[
\frac{dn(m, t)}{dt} = \frac{x}{2} \int_0^m \beta(m_j, m-m_j)n(m-m_j, t)n(m_j, t)dm_j \\
- \alpha n(m, t) \int_0^\infty \beta(m, m_j)n(m_j, t)dm_j - n(m, t) \frac{w_s(m)}{2} + I(m, t)
\]

where \(x\) (the stickiness) is the probability that two particles will stick to each other after they have collided, \(\beta(m, m_j)\) is the coagulation kernel for particle-particle interactions which determines the rate of collision between particles of masses \(m\) and \(m_j\), \(w_s(m)\) is the settling velocity of particles of mass \(m\), and \(I(m, t)\) is the rate of formation of particles of mass \(m\).

To simulate coagulation of multiple particle sources, we based our model on the Stochastic Lagrangian Aggregate Model for Sinking Particles (SLAMS) developed and described by Jokulsdottir and Archer (2016). This is a 1-D model that uses a Monte Carlo approach to simulate the coagulation and disaggregation of marine particles, predicting the evolution of the particle size spectrum with time and depth. To avoid describing every particle in the water column, SLAMS employs the concept of a "super particle" to represent
an aggregate class (AC), a simulated particle that represents a large and variable number of real particles with similar properties. This allows us to describe both highly abundant, small particles as well as rarer large particles within the same simulation. The original SLAMS model simulates the coagulations and settling of different types of phytoplankton cells (coccolithophorids, diatoms, picoplankton) with dust particles and TEP. To simulate the formation of MOS we have made the following modifications to the model.

2.1. Adding Oil and Sediment Particles
We added two new particle types to the model, oil and river sediments. Both interact with the abundant biological particles in the surface water promoting the formation of MOS aggregates. Oil was brought to the shallow waters from the deeper layers as rising droplets originating from the under water releases. In addition, the surface breaking waves also entrain oil droplets into the water from the surface slicks. The river outfalls are the main source of sediments into the surface ocean waters. Both the DWH and IXTOC-1 spills in the Gulf of Mexico occurred near deltaic systems and enhanced river flow during the incidents brought heavy sediment loads to the sites (MOSSFA Report, 2014). Including sediment particles in the simulation is important because they provide a ballasting effect that allows MOS aggregates to sink in the water column.

The model was configured to define oil and sediment introduced as individual particles or as a cluster of primary particles in an aggregate. Parameters for oil and sediment (e.g., the density, stickiness, and particle size distribution) are defined as inputs in the model. Typical values of particle densities used in the simulation are 850 kg m$^{-3}$ (Spaulding et al., 2015) and 1,200 kg m$^{-3}$ for oil and sediment, respectively. Stickiness values for different components in aggregates are defined in section 2.2. The size distributions of aggregates are specific to different locations.

2.2. Modeling Disaggregation
Aggregate disintegration plays an important role in shaping the particle size distribution. Jackson (1995) showed the necessity of including disaggregation in coagulation models in order to reproduce experimental observations of aggregation in a mesocosm. Different processes can contribute to particle breakup, including erosion and splitting by fluid shear (Parker et al., 1971), and breakup by swimming zooplankton (Dilling & Alldredge, 2000). The original SLAMS model determines aggregate breakup rates based on the zooplankton encounters with the aggregates and the stickiness of aggregates. Stickiness is taken as a function of the volumes of different marine snow components and is dependent on their age and dissolution. However, we have little information on the interaction between zooplankton and marine snow in the presence of oil, and so we described aggregate breakup in terms of fluid shear and stickiness defined in section 2.2.

In the model, aggregate breakup occurs if either of the following criteria are satisfied: (1) the size of the aggregate is larger than the Kolmogorov length scale $\eta = (\nu^3 / \epsilon)^{1/4}$, where $\nu$ is the fluid kinematic viscosity and $\epsilon$ is the energy dissipation rate, and (2) aggregate stickiness $<0.02$ (Jokulsdottir & Archer, 2016). The kinematic viscosity of the water is calculated from the dynamic viscosity ($\nu = \nu \rho_w$ where $\rho_w$ is the density of water) based on seawater properties (section 2.3). The energy dissipation rate in W kg$^{-1}$ is calculated as $\epsilon = 5.82 \times 10^{-9} U_{w}^{3}$ (Jackson, 2001; MacKenzie & Leggett, 1993). Aggregates are assumed to breakup into two, similar-sized fragments, as in previous models (Jackson & Burd, 1998; Li et al., 2004), because there is very little information on the size distribution of daughter particles, with or without the presence of oil. Currently, existing oil and gas far-field models also do not consider the breakup of pure oil droplets.

2.3. Seawater Properties
Sea water properties vary with depth in the model and are used to calculate the variation of dynamic viscosity. The density is estimated using standard formulae (Gill, 1982) and the dynamic viscosity is calculated based on seawater properties (section 2.3). The energy dissipation rate in W kg$^{-1}$ is calculated as $\epsilon = 5.82 \times 10^{-9} U_{w}^{3}$ (Jackson, 2001; MacKenzie & Leggett, 1993). Aggregates are assumed to breakup into two, similar-sized fragments, as in previous models (Jackson & Burd, 1998; Li et al., 2004), because there is very little information on the size distribution of daughter particles, with or without the presence of oil. Currently, existing oil and gas far-field models also do not consider the breakup of pure oil droplets.

2.4. Settling Velocity of Aggregates
The original SLAMS model uses the Stokes’ Law with White’s approximation to estimate the settling or rising velocities of aggregates. Here we introduce a modified version of the same formulation (Yick et al., 2009) which accounts for the effects of stratification on the drag coefficient ($C_D$) for low Reynolds numbers. Accordingly the aggregate velocity is estimated by
\[ V^2 = \frac{4g\delta_a (\rho_g - \rho_a)}{3C_d \rho_a} \]  
(1)

\[ C_d = \left[ \frac{24}{Re} - \frac{6}{1 + \sqrt{Re}} + 0.4 \right] [1 + 1.9R_i^{1/2}] \]  
(2)

where \( V \) is the aggregate settling/rising velocity (m s\(^{-1}\)), \( g \) is the gravitational acceleration (m s\(^{-2}\)), \( \delta_a \) is the aggregate diameter (m), the Reynolds number is \( Re = V\delta_a / v \), \( \rho_a \) is density of aggregate (kg m\(^{-3}\)), the viscous Richardson number is \( R_i = de N_r^2 / (\gamma V) \) and \( N_r = -(g/\rho_a) d\rho/dz \) is the buoyancy frequency (s\(^{-1}\)), \( \rho_a \) is a reference fluid density (kg m\(^{-3}\)), and \( d\rho/dz \) is background density gradient. The effect of the enhanced drag can increase settling times in aquatic environments with strong stratification affecting the vertical fluxes of matter (Yick et al., 2009).

### 2.5. Aggregate Fractal Dimension

The fractal dimension of an aggregate arises from the scaling relationship between aggregate mass and size and is a measure of aggregate structure and porosity. Aggregates with a fractal dimension of 3 have a mass that scales with the length cubed and are compact objects that are either solid or have a constant porosity. Particles with fractal dimensions less than 3 have a higher porosity which increases with particle size, creating larger and more extended particles (for the same mass) (Burd & Jackson, 2009; Laurenceau-Cornec et al., 2015; Logan & Wilkinson, 1990). Typical fractal dimensions estimated for marine aggregates from different locations fall within the range of 1.3–2.3 (Burd & Jackson, 2009; Logan & Kilps, 1995). We follow the original SLAMS models and use a fixed aggregate fractal dimension. We determined the value using model calibration simulations that were carried out to obtain a best fit of the model predicted particle size spectrum with the measured field data from the Gulf of Mexico during the DWH spill (section 4).

### 2.6. Aggregate Stickiness

The value of the stickiness parameter (\( \alpha \)) plays an important role in both particle aggregation and disaggregation process (Mari & Burd, 1998). It is usual in marine coagulation models to use a single value for the stickiness of all particles. This assumes that particle composition is homogeneous and does not change with particle size or depth. However, different particle types in a system may have different values of stickinesses depending on their composition and other properties, such as the morphology, but the main controls on the particle stickiness in the marine particle are not well understood (Burd & Jackson, 2009). In addition, measurements of stickinesses for different types of particles in a system are limited. However, it is thought that TEP is the main “glue” that holds particles together (Mari et al., 2017; Passow et al., 2001). Building on the original SLAMS model, we calculate aggregate stickiness (\( S_{\text{agg}} \)) as a function of the volume fractions of TEP (\( V_{\text{TEP}} \)), organic carbon (\( V_{\text{OrgC}} \)), oil (\( V_{\text{Oil}} \)), and sediment (\( V_{\text{Sed}} \)), and their individual stickinesses as

\[ S_{\text{agg}} = (A V_{\text{OrgC}} + V_{\text{TEP}} + S_{\text{Dgr}} V_{\text{Oil}} + S_{\text{Sed}} V_{\text{Sed}}) / V_{\text{agg}} \]  
(3)

The individual stickiness values \( S_{\text{TEP}} \), \( S_{\text{OrgC}} \), \( S_{\text{Oil}} \), and \( S_{\text{Sed}} \) are defined as 0.8, 0.08, 0.3, and 0.6, respectively, based on the ranges found in the literature (Mari et al., 2017; Sterling et al., 2005). The variation of these values with their degradation and age (Mari et al., 2017) is not considered due to lack of understanding of these processes to implement in the model. Because equation (3) is somewhat ad hoc, and there are no existing models for the stickiness of a heterogenous aggregate, we used two additional formulations for aggregate stickiness to investigate the sensitivity of the model results. In the first case, we assumed that aggregate stickiness depended only on the volume fractions of organic carbon and TEP

\[ S_{\text{agg}} = (A V_{\text{OrgC}} + V_{\text{TEP}}) / V_{\text{agg}} \]  
(4)

where \( A = 0.1 \) is a constant that was defined in Jokulsdottir and Archer (2016). The third model we assumed that the same components contributed to stickiness as in equation (3), but that each contributed equally to the overall stickiness depending on their volume fraction

\[ S_{\text{agg}} = (V_{\text{OrgC}} + V_{\text{TEP}} + V_{\text{Oil}} + V_{\text{Sed}}) / V_{\text{agg}} \]  
(5)

### 3. Field Data Collected During the Deepwater Horizon Spill

Marine snow distributions in near-surface waters were assessed on a Natural Resource Damage Assessment (NRDA) cruises between 28 May and 3 June 2010 using SIPPER camera imaging system in the vicinity of the
The exact composition of marine snow particles during and after the DWH spill is not known. We do know that a particularly large diatom
bloom of *Skeletonema* sp. produced a large, sustained pulse of sinking material (Yan et al., 2016). We also know that enhanced outflow from the Mississippi may have led to increased concentrations of mineral particles offshore (Vonk et al., 2015), but concentrations of mineral particles in the water column from that time are not available. We know that TEP plays an important role in MOS formation but we know little about what controls its production rate in these circumstances (Quigg et al., 2016). We have better estimates of the amount of oil in the surface waters during the DWH spill. MacDonald et al. (2015) report surfacing oil volume flux estimates based on satellite images which we used to obtain an order of magnitude estimate of oil on the surface and to check the input of oil into the surface layers in the simulations. For the five stations, the MacDonald et al. (2015) estimated surfacing oil fluxes vary between about 6 and 14 g week$^{-1}$ m$^{-2}$. Predictions from deepwater oil and gas blowout plume models (Dissanayake et al., 2018; Johansen, 2000; Spaulding et al., 2000; Yapa & Li, 1997) can be used to calculate the oil in the water column, in intrusions, and on the surface. Spaulding et al. (2015) estimated that total insoluble hydrocarbon into the deep plume was $1.09 \times 10^6 \pm 1.422 \times 10^5$ during the DWH spill and Gros et al. (2017) estimates that about 73% petroleum mass remained in the water without dissolving in the days after the fallen riser was removed from the wellhead. Without further information we amended the list of marine snow components included in the SLAMS model to include the following: diatoms, picoplankton, fecal pellets, TEP, river sediments, and oil. To assess the affect of our choices, we ran the simulations using two initial compositions shown in Table 2 that were used as inputs in the top 5 m of the water column. The different components of marine snow were added to the system with the same probability ratios defined in the SLAMS model such that they added up to the total mass fractions shown in Table 2. The size distribution of the input
aggregates was assumed to be the measured distributions from NRDA data in the surface 5 m depth of the water column and each aggregate of different sizes was assumed to have the composition given in Table 2.

4.2. Model Calibration and Validation

Marine snow particle size distributions are sensitive to the fractal dimension because they have a nonlinear effect on particle sizes, collision rates, and settling velocities. Estimates of the fractal dimension of nonoil associated marine snow vary between 1.3 and 2.3 (Burd & Jackson, 2009), but we have no estimates of the fractal dimensions of MOS. To determine a value, we compared size spectra modeled using a range of fractal dimensions with those observed at GG01, comparing modeled and predicted size spectra in different depth layers to a maximum depth of 200 m. Based on these initial comparisons we chose a fractal dimension of 2.2 for the MOS aggregates. Then the model simulations were carried out at the stations GG002, GG003, GG004, and GG005 using the fixed fractal dimension of 2.2 and with the composition shown in Table 2 to study the models performance with input parameters at each station.

5. Model Results

5.1. Particle Size Spectra

We compared the modeled and observed size spectra by averaging both over five depth bins: 0–40, 40–80, 120–160, 160–200, and 560–600 or 1,160–1,200 m. This was done in part because of the large variability between nearby depth bins in both observed and modeled spectra. In general, the modeled and observed size distributions show reasonable agreement, but with some notable exceptions (Figures 4–6). Modeled and observed size spectra in deeper waters have fewer small particles, indicative of aggregate formation. Neither observed nor modeled spectra show a consistent trend with depth or distance from the wellhead. Quantitative comparison between modeled and observed spectra can be made using the slope of the log-transformed size spectra (Table 3) over the size range $10^2$–$10^4$ µm. This size range removed the modeled large particles that are an artifact of our disaggregation model from the calculation of the slopes. The slopes of approximately half the modeled spectra agree with the observed slopes to within the stated uncertainties, though in general, the slopes of the modeled size spectra were less steep than the observed slopes. Modeled size spectrum slopes at GG03 are smaller than for the other sites, though curiously this site shows the steepest slope in the 40–80 m depth range in the observed spectra. Using input particle composition 2 (Table 2) produced spectra with slopes that did not match the observed slopes quite as well as those obtained using input particle composition 1. Removing disaggregation from the model produced size spectra with less scatter, but were generally significantly less steep than those including disaggregation.

5.2. Oil Fluxes

The total modeled oil flux reaching the seafloor reaches a steady state after about 5 weeks for all the five locations, although the steady state oil fluxes vary between sites (Figures 7 and 8). Sites GG01, GG04, and GG05 have modeled oil fluxes between 0.25 and 0.42 g week$^{-1}$ m$^{-2}$. Again, site GG03 is the outlier, with an oil flux of 10.24 g week$^{-1}$ m$^{-2}$. Increasing the percentage of oil in the input aggregates did not always lead to an increase in the steady state flux of oil to the seafloor (Table 4). The flux of oil increased by 3–44% at sites GG01, GG02, and GG03, but decreased the flux of oil at the seafloor by 7% and 11% at sites GG04 and GG05.

5.3. Particle Composition

The composition of particles, and hence their properties such as settling velocity, change over time in the model as particles aggregate and disaggregate. This is shown in Figure 9. The average terminal velocity of particles is initially negative, indicating that the presence of oil in the aggregate dominates the settling velocity. However, as ballast materials (e.g., sediment particles, etc.) combine with the oil to form new aggregates, the average aggregate density increases and the average terminal velocity becomes positive, eventually settling at a value between 30 and 40 m d$^{-1}$. Because this is a stochastic simulation, the average
Figure 4. Comparison of the model predicted (filled dots and plus sign) and the measured (open dots) aggregate size spectrum at the stations GG01–GG05 in different depth layers using composition 1 (Table 2). Each row represents a single station with GG01 at the top and GG05 at the bottom.
Figure 5. Comparison of the model predicted (filled dots and plus sign) and the measured (open dots) aggregate size spectrum at the stations GG01–GG05 in different depth layers using composition 2.
Figure 6. Comparison of the model predicted (filled dots and plus sign) and the measured (open dots) aggregate size spectrum at the stations GG01–GG05 in different depth layers using composition 1 with no breakup of aggregates.
velocity fluctuates as both the composition and average size of the aggregates in the water column fluctuate over time.

### 5.4. Model Sensitivity Analysis

The sensitivities of the modeled seafloor flux to variability in the fractal dimension and stickiness are shown in Figure 10. All these simulations are carried out up to a depth of 1,500 m so that the maximum depth

![Figure 7](image-url)

**Figure 7.** Settling fluxes of total aggregate masses and oil at the seafloor for the simulations with composition 1 at stations GG01–GG05.

<table>
<thead>
<tr>
<th>Table 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Slope of the Aggregate Size Spectrum at Different Depths and Stations as Shown in Figure 4; Uncertainties Are 1 Standard Deviation</strong></td>
</tr>
<tr>
<td>Depth</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>GG01 Model A</td>
</tr>
<tr>
<td>Model B</td>
</tr>
<tr>
<td>Model C</td>
</tr>
<tr>
<td>Data</td>
</tr>
<tr>
<td>GG02 Model A</td>
</tr>
<tr>
<td>Model B</td>
</tr>
<tr>
<td>Model C</td>
</tr>
<tr>
<td>Data</td>
</tr>
<tr>
<td>GG03 Model A</td>
</tr>
<tr>
<td>Model B</td>
</tr>
<tr>
<td>Model C</td>
</tr>
<tr>
<td>Data</td>
</tr>
<tr>
<td>GG04 Model A</td>
</tr>
<tr>
<td>Model B</td>
</tr>
<tr>
<td>Model C</td>
</tr>
<tr>
<td>Data</td>
</tr>
<tr>
<td>GG05 Model A</td>
</tr>
<tr>
<td>Model B</td>
</tr>
<tr>
<td>Model C</td>
</tr>
<tr>
<td>Data</td>
</tr>
</tbody>
</table>

**Note.** Model A uses input particle concentration 1 and includes disaggregation, Model B uses input particle concentration 2 and includes disaggregation, Model C uses input particle concentration 1 and does not include disaggregation.
aggregates vertically travel is the same for all the cases. The model is extremely sensitive to particle fractal dimension with a relative variation in seafloor flux ranging from almost −80% to +80%. Lower values of the fractal dimension reduced the flux to the seafloor, whereas increasing the fractal dimension generally led to increases in the flux, the outlier being the station GG02 where increasing the fractal dimension led to a decrease in flux at the seafloor.

6. Discussion

Large aggregates of marine snow and oil have been observed in the water column after large oil spills (Passow, 2016; Passow et al., 2012) and contribute to sedimentation of oil (Passow & Ziervogel, 2016) in MOSSFA (Marine Oil Snow Sedimentation and Flocculant Accumulation) events. The formation and sinking of MOS provide a pathway for the removal of oil from the water column that is not often considered when determining strategies for responding to oil spills (Daly et al., 2016; MOSSFA Report, 2014). Estimates of the amount of oil that sank to the seafloor during the Deepwater Horizon oil spill vary from 3% to 31% (Chanton et al., 2014; Stout et al., 2017; Valentine et al., 2014; Yan et al., 2016). Given this variability, and the potentially significant amount of oil sinking to the seafloor, it is important to understand the processes affecting MOS formation and the occurrence of MOSSFA events, as well as to have predictive models of the fate of oil spills that incorporate these processes for developing appropriate response strategies and determining mass budgets for spilled oil.

Coagulation theory is well established as a basis for modeling marine snow formation and sedimentation (Jackson, 1990; Jackson & Burd, 1998). In addition, the aggregation of oil with mineral particles to form mineral-oil-aggregates has been studied for a long time (Bandara et al., 2011; Gong et al., 2014; Khelifa et al., 2002, 2005; Lee, 2002; Zhang et al., 2012; Zhao et al., 2016). However, the problem of aggregation of oil with marine snow has seen less attention. The model we have presented here is an attempt to use what we know about modeling marine snow formation to understand the factors affecting MOS formation and MOSSFA events. Although the model presented here reproduces observed size spectra reasonably well, there are several factors that are uncertain and which affect the accuracy of the model.

Table 4
Bottom Settling Fluxes of Oil for Composition 1 and Composition 2

<table>
<thead>
<tr>
<th>Station</th>
<th>Composition 1 (g week$^{-1}$ m$^{-2}$)</th>
<th>Composition 2 (g week$^{-1}$ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GG01</td>
<td>0.31</td>
<td>0.32</td>
</tr>
<tr>
<td>GG02</td>
<td>1.14</td>
<td>1.65</td>
</tr>
<tr>
<td>GG03</td>
<td>10.36</td>
<td>14.89</td>
</tr>
<tr>
<td>GG04</td>
<td>0.26</td>
<td>0.25</td>
</tr>
<tr>
<td>GG05</td>
<td>0.42</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Figure 8. Settling fluxes of total aggregate masses and oil at the seafloor for the simulations with composition 2 at stations GG01–GG05.
The model is sensitive to the fractal dimension of the particles. The fractal dimension has a maximum value of 3 and characterizes the geometric structure of the aggregate, with larger values corresponding to more solid objects (Meakin, 1998). For an aggregate of a given mass, the fractal dimension affects the size of the aggregate, its density, and settling velocity—and therefore its frequency of collisions with other particles—all in a nonlinear manner. We chose a value of 2.2 for the aggregate fractal dimension based on comparing model results with observed size spectra at a single station. Reported fractal dimensions for non-oil associated marine snow range from 1.3 to 2.3 (Burd & Jackson, 2009) making the value we used at the higher end of this range. Our results indicate the possibility that including oil into an aggregate may alter how compact the aggregate is. This is hard to determine without further laboratory and numerical experiments. The aggregation process itself is also known to change the fractal dimensions of aggregates, with the typical fractal dimension of aggregates decreasing over time as aggregates collide to form larger particles (Chakrabarti et al., 2003). Numerical simulations indicate that the size distribution of the primary particles probably does not have much of an impact on the fractal dimensions of the particles (Bushell & Amal, 1998) but the shape of the primary particles does have a significant effect (Perry et al., 2012), with ellipsoidal monomers forming aggregates having lower fractal dimensions than those created using spherical monomers. However, the effect of the nature of the primary particles on the shape and characteristics of the final aggregate have rarely been studied. Given the shapes of the particles comprising marine snow (e.g., fecal pellets, diatoms, diatom chains, etc.), this may be important. Capillary bridging between marine snow particles by oil droplets may also affect packaging within an aggregate and its fractal dimension (Strauch & Herminghaus, 2012).

Our model results are also sensitive to the way in which stickiness is calculated, though to a lesser degree than the fractal dimension. Stickiness is important because it not only determines the probability of adhesion once a collision between two particles has occurred, it also plays a role in determining the structure of the aggregate. Particles with high stickiness tend to stick on their first collision and create highly porous particles—for small particles, this is called diffusion-limited-aggregation (Meakin, 1998). Conversely, particles with low stickiness tend to collide many times before adhering, and this allows...
for the possibility that two particles will mesh together creating a more compact aggregate (so-called reaction-limited-aggregation). Most simulations of marine snow formation assume a constant stickiness for all particles. In reality, particles will have different adhesion probabilities resulting in aggregates of different compositions (Sterling et al., 2004, 2005). However, currently no model assumes stickiness of a heterogeneous aggregate composed of mineral and organic material, although estimates of the stickiness for individual types of particles have been estimated (Mari et al., 2017; Sterling et al., 2004). The strength of aggregates has also been seen to change with age (Alldredge et al., 1990) and we might expect that biodegradation will affect the particle stickiness (Yamada et al., 2013). The model we have used assumes that each component of an aggregate has a uniform stickiness and that the stickiness of an aggregate is a volume weighted average of the stickiness of all the components. One might suspect that an average weighted by surface area would be more appropriate, because particles interact through their surfaces. However, the contact area between individual components of an aggregate is very difficult to track. In the simulations, the total stickiness coefficients of aggregates varied between 0.29 and 0.36 over time.

Our model produced a higher concentration of very large (>1 cm) particles than was observed in the field data. This was a result of the way we modeled disaggregation. There are two main mechanisms of particle breakup that are usually considered, breakup by fluid shear (Parker et al., 1971) and by swimming zooplankton (Dilling & Alldredge, 2000; Turner, 2015). Disaggregation affects not only the abundance of large particles, but also smaller particles (Burd & Jackson, 2002). This is because disaggregation increases the concentrations of smaller particles. Because coagulation rates depend quadratically on the particle concentration, disaggregation also increases the coagulation rates of daughter particles with those around it. Disaggregation of marine particles is hard to model for several reasons. First, we do not have a good understanding of the factors controlling the strength of marine snow aggregates. Measurements indicate that marine flocs of biological origin are resistant to typical marine fluid shears, and that the strength of the more fragile diatom flocs increases with age (Alldredge et al., 1990). Second, the size spectrum of particles created when an aggregate breaks up is unknown. Hill (1996) followed Pandya and Spielman (1982) in assuming that the sizes of created particles are normally distributed. Jackson (1995) and Stemmann et al. (2004) incorporated two extreme cases into their models: aggregates breakup into two similar-sized particles or breakup into a cloud of monomer particles. One might expect different disaggregation processes to operate in different parts of the water column. For example, higher fluid shears are found in the surface waters, whereas deeper in the water column, mechanical breakup by swimming and feeding zooplankton may dominate. Each of these processes might be expected to produce a different size distribution of small particles. To make matters more complicated, we have little understanding of how oil will affect the size distribution of particles created by disaggregation. One might expect that oil contained in an aggregate might increase the strength of the particle. The model we have used is simple, and captures breakup into similarly-sized particles which may be more relevant for mechanical breakup by zooplankton swimming.

Dispersants are a frequently used in marine oil spills to breakup oil droplets. During the Deepwater Horizon Spill Corexit9500A was used to disperse oil in the surface waters and near the wellhead. This will obviously affect the particle size distribution of oil droplets, and may also affect the overall formation of MOS. Some studies have indicated that both oil and dispersant can promote the formation of MOS (Fu et al., 2014), however Passow et al. (2017) have shown that the presence of oil can promote MOS formation, but oil dispersed using the dispersant Corexit inhibits aggregation by also dispersing TEP. We have not yet included the effects of dispersant into our model. This could be done by adjusting the properties of the oil and TEP input into the model, but any improvements in model accuracy would be outweighed by existing uncertainties in fractal dimension, stickiness, and disaggregation.

Under steady state conditions, the total amount of oil in the water column using both input compositions were comparable with estimates of oil in the water column during the Deepwater Horizon spill. Approximately 6×10^8 kg of oil was released into the far-field during the oil spill (TAMOC simulations-https://doi.org/10.7266/N7F47M4Q). If we assume that the oil spread uniformly throughout the water column with an area of 10^4 km^2, this gives a depth-integrated water column oil concentration of 60 g m^-2. Modeled depth-integrated water column concentrations of oil varied from 13 to 50 g m^-2.
for stations GG01, GG02, GG04, and GG05 which are of a similar order of magnitude—using a slightly larger area would make the agreement better. Simulations at GG03 produced water column concentrations of oil that were much higher, 242 g m\(^{-2}\) for input concentration 1 and 355 g m\(^{-2}\) for input concentration 2.

Not all the oil in the water column settled to the seafloor. Estimates of the total amount of oil that settled to the seafloor during the Deepwater Horizon spill vary. Stout and German (2017) use a deepwater footprint of 1,030 km\(^{2}\) and estimate that the oil concentration on the seafloor was 20 g m\(^{-2}\). Romero et al. (2017) used a larger deep-sea area, 32,648 km\(^{2}\), covering depths between 200 and 2,600 m, and estimated that 0.039–0.098 g m\(^{-2}\) of oil settled on the bottom, but within an area of 219 km\(^{2}\), 2.39–8.74 g m\(^{-2}\) was deposited. Over a 12 week period (the Deepwater Horizon spill lasted from 20 April 2010 to 15 July 2010), the accumulated oil deposited on the seafloor in the model varied from 3.0 to 19.8 g m\(^{-2}\), excluding station GG03 where the total deposited oil was almost two orders of magnitude higher. These values compare well with the admittedly wide range of values deduced from sediment analysis. Changes in the composition of the input particles affected the composition of material settling on the seafloor. Using composition 2 produced a 7% and 11% reduction in the flux of oil at the seafloor compared to using input composition 1 for stations GG04 and GG05, respectively, while composition 2 increased fluxes by 3% at station GG01 and 44% at stations GG02 and GG03. The controlling factor in these three cases was the increase in ballast in the input composition. Comparing modeled and observed particle size spectra and settling rates at the seafloor, we know that GG03 is a very different site than the other four stations. Main reason for this appears to be that the number of aggregates on the surface layer is approximately twice at that the other stations (Figure 3). This high number concentration of particles leads to faster aggregation and settling rates than at other stations. This explains the higher seafloor settling rates predicted from the model at station GG03. Station GG02 which has the next highest aggregate number concentration on the surface has the second highest predicted bottom settling rates.

Differences between the model predicted and observed aggregate size distribution may be due to other factors apart from the internal model parameters mentioned in the sensitivity analysis. The aggregate size distribution observations were made at a fixed time over a single depth profile. However, because of their finite settling speeds, aggregates at different depths reflect size distributions at the surface at earlier times. But our model assumes a steady state and without observations over time at a single location it is hard to know how the surface size distributions varied over time. The lack of variation of size distributions at the surface layers with time in the model makes it difficult to model spectra at depth accurately. The large variation in the measured and model predicted size distributions at station GG03 may have resulted from this. The large number of surface aggregates in the surface measurements may not be reflected in the aggregate sizes observed in the deeper layers at the same location. Similarly, horizontal advection is not taken into account in the present model but can be a significant factor that will transport aggregates horizontally while they settle in the water column. Aggregates deeper in the water column could come from surface regions that are far from the location of the observed depth profile (Siegel & Deuser, 1997).

### 7. Conclusions

Given the uncertainties in parameterizing stickiness, disaggregation, and assigning fractal dimensions to the aggregates, we believe the model shows reasonable agreement with observed size spectra and deposition rates of oil on the seafloor. Ideally we would like to be able to model the time evolution of oil and MOS in the water column. This will involve coupling the model to the output of a hydrodynamic model that will allow us to simulate how oil and MOS are advected within the system. Additional research on the factors controlling aggregate structure, stickiness, and disaggregation rates will undoubtedly improve the comparison with data.

### Appendix A: Equations for Density and Dynamic Viscosity

Seawater density, \(\rho_{sw}\), is calculated as
\[ P_{sw} = \frac{P_{sw0}}{1 - \frac{P}{K}} \]
\[ P_{sw} = \frac{(999.842594 + 6.793952 \times 10^{-3}T^2 - 9.095290 \times 10^{-3}T^3 + 1.001685 \times 10^{-4}T^4 - 1.20083 \times 10^{-6}T^5 + 6.536332 \times 10^{-9}T^6 + 8.24493 \times 10^{-1}S^2 - 5.72466 \times 10^{-2}S^2 + 4.8314 \times 10^{-4}S^2 - 4.0899 \times 10^{-7}T^2S + 7.6438 \times 10^{-5}T^2S - 8.2467 \times 10^{-7}T^2S + 5.3875 \times 10^{-9}T^4S + 1.0227 \times 10^{-4}T^4S + 1.6546 \times 10^{-6}T^2S^2)}{(19652.21 + 148.4206T - 2.327105T^2 + 1.360477 \times 10^{-2}T^3 - 5.155288 \times 10^{-5}T^3 + 3.239908P + 1.43713 \times 10^{-3}TP + 1.16092 \times 10^{-4}T^2P - 5.77905 \times 10^{-7}T^3P + 8.50935 \times 10^{-9}P^2 - 6.12293 \times 10^{-6}P^3 + 5.2787 \times 10^{-8}T^2P^2 + 54.67465 - 0.603459TS - 1.09987 \times 10^{-2}T^2S - 6.1670 \times 10^{-5}T^3S + 7.944 \times 10^{-2}S^3 + 1.64833 \times 10^{-7}T^2S^2 - 5.3009 \times 10^{-4}T^2S^2 + 2.2838 \times 10^{-3}TP - 1.0981 \times 10^{-5}TPS - 1.6078 \times 10^{-6}T^2PS + 1.91075 \times 10^{-4}PS^2 - 9.9348 \times 10^{-7}P^2S + 2.0816 \times 10^{-8}TP^2S + 9.1697 \times 10^{-10}T^2P^2S)} \]
(A1)

where \( P \) is pressure in bar, \( T \) is temperature in Celsius, and \( S \) is salinity at the calculation location.

Dynamic viscosity, \( \mu \) is calculated as

\[ \mu = \mu_0 \left( 0.9994 + 4.0295 \times 10^{-5}P_c + 3.1062 \times 10^{-8}P_c^2 \right) \]
(A2)

\[ P_c = 0.00014503773800721815P_0 \]
(A3)

\[ \mu_0 = \mu_w \left( 1 + A S_c + B S_c^2 \right) \]
(A4)

\[ S_c = S/1000 \]

\[ A = 1.5409136040 + 1.9981117208T - 9.5203865864 \times 10^{-3}T^2 \]

\[ B = 7.9739318223 - 7.5614568881 \times 10^{-1} - 2T + 4.7237011074 \times 10^{-4}T^2 \]

\[ \mu_w = 4.2844324477 \times 10^{-5} + 1/1.5700386464 \times 10^{-1} \left( T + 6.4992620050 \times 10^1 \right)^2 - 9.1296496657 \times 10^1 \]
(A5)

(A6)

where \( P \) is pressure in Pascal, \( T \) is temperature in Celsius, and \( S \) is salinity at the calculation location.

Acknowledgments

This research was made possible by a grant from The Gulf of Mexico Research Initiative to support the Project: Oil-Marine Snow-Mineral Aggregate Interactions and Sedimentation during the 2010 Deepwater Horizon Oil Spill. Data are publicly available through the Gulf of Mexico Research Initiative Information & Data Cooperative (GRIIDC) at https://data.gulfresearchinitiative.org. Simulation results are at https://doi.org/10.7266/N73R0R7S and field data used for the validations are at https://doi.org/10.7266/N779437K. We would like to thank Tinna Jockulsdottir for making her code available to us. We also thank A. Remsen for the NRDA field data, K. Kramer for size-frequency analyses of marine snow, and K. Dubikas for creating Figure 1.

References


